POLYSULFONE MIXED MATRIX MEMBRANES WITH BIOSYNTHESIS NANOPARTICLES: ENHANCEMENT OF INTERFACE COMPATIBILITY AND ANTIBACTERIAL MEMBRANE SEPERATION PROCESS

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For my beloved mother and father

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ABSTRACT

This study investigates the effect of biosynthesis silver nanoparticles (bio-AgNPs) structure towards PSf membranes performance. The addition of bio-AgNPs in the membrane formulation was aimed to improve antibacterial properties and interface compatibility of the polymer mixed matric membrane. In this work, facile green synthesis method of silver nanoparticles was prepared using *Parkia speciosa* (Petai) leaves extract silver nitrate aqueous solution. The bio-AgNPs/PSf membranes was fabricated using phase-inversion process. Characterization of the synthesized bio-AgNPs and mixed matrix membranes via UV-Vis spectroscopy (UV-Vis), Field emission scanning electron microscope (FESEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). Surface plasmon resonance for bio-AgNPs was assigned at 465 nm with brown colour. FTIR spectroscopy identified the biomolecules capped on the surface of nanoparticles are phenol, flavonoid and terpenoid compounds. The microstructure and structural analyses had shown that AgNPs possessed good characteristics with spherical shapes, small average size of particles (59.96 nm), and small crystallite size. The bio-AgNPs also showed significant potential antibacterial activity against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). The addition of bio-AgNPs was able to enhance the hydrophilicity of composite PSf membranes which proved by decreasing the value of contact angle. Meanwhile, structure on bottom layer shown a porous bulk with finger-like structure and macroviod structure which is responsible for mechanical support. Finger-like structure on top layer became smaller with increment of bio-AgNPs because of its hydrophilicity properties. Hence, the pure water flux also will increase because the hydrophilicity properties was an essential factor for water permeability. The molecular interaction between molecules was investigated using Dynamic mechanical analysis (DMA) and silver leaching analysis by Inductive coupled plasma mass spectrometer (ICP-MS).

As revealed, the strength of molecular interaction between AgNPs and PSf molecules was improved with addition of bio-AgNPs. Hence, overall the results showed that the incorporation of bio-AgNPs able to improve antibacterial properties and interface compatibility of the polymer mixed matric membrane.

ABSTRAK

Kajian ini menyiasat kesan biosintesis perak nanopartikel perak (bio-AgNPs) ke arah prestasi membran PSF. Penambahan bio-AgNPs dalam pembentukan membran bertujuan meningkatkan sifat antibakteria dan keserasian antara muka membran matrik campuran polimer. Dalam kerja ini, kaedah sintetik hijau mudah nanopartikel perak telah disediakan menggunakan estrak daun *Parkia speciosa* (Petai) dan larutan perak nitrat. Membran bio-AgNPs / PSf dihasilkan menggunakan proses fasa penyongsangan. Pencirian bio-AgNPs dan membran matriks campuran melalui spektroskopi UV-Vis (UV-Vis), mikroskop elektron pengimbasan pancaran (FESEM), mikroskop elektron penghantaran (TEM), X-ray difraksi sinar XRD, spektroskopi (FTIR). Resonans plasmon permukaan untuk bio-AgNPs adalah pada 465 nm dengan warna coklat. Spektroskopi FTIR mengenal pasti biomolekul yang dihadkan pada permukaan nanopartikel ialah sebatian fenol, flavonoid dan terpenoid. Analisis mikrostruktur dan struktur telah menunjukkan bahawa AgNP mempunyai ciri-ciri yang baik dengan bentuk bulat, saiz purata zarah kecil (59.96 nm), dan saiz kristal kecil. Bio-AgNP juga menunjukkan potensi aktiviti antibakteria yang signifikan terhadap Escherichia coli (E. coli) dan Staphylococcus aureus (S. aureus). Penambahan bio-AgNPs dapat meningkatkan hidrofililik membran PSF komposit yang terbukti dengan mengurangkan nilai sudut sentuhan. Sementara itu, struktur pada lapisan bawah menunjukkan liang berpori dengan struktur seperti jari dan struktur macroviod yang bertanggungjawab untuk sokongan mekanikal. Struktur seperti jari pada lapisan atas menjadi lebih kecil dengan kenaikan bio-AgNPs kerana sifat hidrofiliknya. Oleh itu, fluks air tulen juga akan meningkat kerana sifat hidrofilik adalah faktor penting untuk kebolehtelapan air. Interaksi molekul antara molekul diselidiki menggunakan Analisis mekanik Dinamik (DMA) dan analisis peleburan perak oleh spektrometer massa plasma bersama Induktif (ICP-MS). Seperti yang dinyatakan, kekuatan interaksi molekul antara molekul AgNPs dan PSF

telah diperbaiki dengan penambahan bio-AgNPs. Oleh itu, secara keseluruhan keputusan menunjukkan bahawa pemerbadanan bio-AgNPs dapat memperbaiki sifat-sifat antibakteria dan keserasian antara muka membran matrik campuran polimer.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
AgNPs	Silver nanoparticles
ASTM	American Society for Testing and Materials
A	Membrane Area (m^2)
Ǻ	Angstrom
C_p	Solute Concentration in permeate stream
C_f	Solute Concentration in Feed
FTIR	Fourier transform-infrared
FESEM	Field Emission Scanning electron microscopy
ICP-MS	Inductive Coupled Plasma Mass Spectrometer
HA	Humic Acid
J_{wf}	Total of pure water flux
J_{cp}	Total of filtration
J_c	Total of pure water flux after physical cleaning
J_a	Total of pure water flux after chemical cleaning
J_O	Pure Water Flux of clean Membrane
J_f	Pure Water Flux of Fouled Membrane
J_f/J_o	Normailzes flux (initial flux / final flux)
LMH	L/m^2. h
MD	Membrane Distillation
MF	Microfiltration
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
PEG	Polyethylene glycol

PWF	Pure Water Flux
PSf	Polysulfone
Q	Permeate volume (L)
R	Rejection of feed components
R_t	Total resistance
R_m	Membrane resistance
R_a	Resistance due to absorption
R_c	Resistance due to cake layer
R_{cp}	Resistance due to cake polarization
RSM	Response surface methodology
RO	Reverse osmosis
SEM	Scanning electron microscope
UF	Ultrafiltration
Wt.%	Weight Percentage
XRD	X-ray diffraction
Δ_t	Time (h)

CHAPTER 1

INTRODUCTION

1.1 Research background

There are various types of water treatment system for eliminating bacteria in water that have been used around the world. Bacteria are found in nearly everywhere in air, water, soil, animals and food. Some bacteria are useful to us and some bacteria are harmful which can cause disease, sickness or other problems. Human needs for clean water in everyday life had led to development of many techniques to eliminate bacteria, such as activated carbon, activated biological filter and the use of membranes in filtration system (Dong *et al.*, 2012). Bacteria separation using membrane technology is an attractive separation approach due to the advantages offered by this process, i.e. high stability and efficiency, ease of operation, low operating cost and energy (Liu *et al.*, 2011).

A membrane separation technology can separate smaller particle as well as able to avoid dangerous contaminate of viruses, fungi and bacteria. Polysulfone membranes (PSf) are known to have superior characteristics by having excellent chemical and thermal stability. Recently, usage of PSf membranes was widely applied in separation fields.

However the main challenge of water treatment by membrane is the fouling phenomena. This phenomena may shorten the membrane service life and reduce the water flux permeation (Zhang *et al*., 2016). Several methods and strategies for membrane fouling control have been developed over the last two decades. The most common method to help reduce fouling of membranes is by modifying the surface of the membranes. Chemical cleaning also controls membrane fouling. Another popular method to control fouling of membrane is by adding inorganic nanoparticles such as Zinc Oxide (ZnO), Titanium Oxide (TiO), Copper (Cu), and Silver (Ag) inside the membrane. These nanoparticles will kill bacterial cells and prevent bacterial attachment to membrane surfaces, which reduce the membrane fouling (McCloskey *et al*, 2010).

The effect of additive towards membrane performance is very important in membrane separation. For example, silver is mixed with the membrane because it can enhance the antibacterial properties. Silver nanoparticles are one of the most important materials with diverse applications. Silver is insoluble in water, which is widely used as an additive in numerous materials and product. It occurs naturally, but most of silver nanoparticles is produced synthetically. In this study, silver was produced by synthesis method using leaf extract of *P. speciosa*. Biosynthesized silver nanoparticles (bio-AgNPs) was added to Polysulfone (PSf) membranes in order to investigate the antibacterial properties of the membranes. The leaf extract was used as reducing and stabilizing agent to synthesize silver nanoparticles at room temperature protocol. *P. speciosa* has high composition of reducing agents such as saponins, flavonoids and terpenoids (Kassim *et al*., 2011). Besides, its antibacterial properties and also abundantly available in Asian countries (Wonghirundecha *et al*., 2014). The effect of bio-AgNPs concentration towards membrane characteristic and performance was evaluated using permeability, rejection and antibacterial properties of the membrane.

1.2 Problem statement

Clean and healthy water are essential and important things in our daily life nowadays, since most water supply is contaminated with various unwanted and pollutants materials. Therefore, the used of membrane technology that able to filter various size of inorganic and organic materials including bacteria, is essential to various application of wastewater treatment. The used of polymer membrane is more favourable compared to the other types of materials as this membrane offer better processing technique, easy to handle during fabrication and operation as well as low price. PSf membranes have been known to be used in various industrial processes due to their advantages of high chemical resistance stability and tolerance of a wide range of pH.

However, polymer membrane always exposed to the bacteria growth that absorb onto membrane surface during separation process. Therefore, the addition of antibacterial agent in the membrane formulation offer a good alternative in order to improve antibacterial properties as well as membrane performance (Leberknight *et al*, 2011). As was reported by Sawada *et al*. (2012), the addition of silver particle is able to eliminate or kill almost 99.99 % of E.coli bacteria. Therefore, the silver nanoparticles will be used in this study as an antibacterial agent to prevent the bacteria growth on membrane. Previous study by Procek *et al*. (2011), which shows that silver is a great antibacterial agent when added into membrane formulation. Basri *et al*., on her investigation confirmed that, most bacteria died with the application of 1 mg Ag/L AgNPs (Basri *et al*., 2010). Even the used of most additives are able to improve membrane properties and performance, the fact that this inorganic particle has different structure easily create compatibility issue that caused leaching of particles problem. This leaching of silver definitely toxic to human as well as to the environment and aquatic system (Nowack *et al*., 2012). Therefore the used of biosynthesis particles that able to provide an organic layer which similar and match well with polymer matrix is a good approach in avoiding the leaching of particles problem. The small inorganic particles encapsulated with organic layer surely can bind strongly with the polymer matrix. In fact the biosynthesis technique are seen currently as a sustainable alternative to replace the synthetic chemical laboratory process.

Therefore, in this current work, the silver nanoparticles was synthesized using leaf extract that functioning as reducing and stabilizing agent. As proven in this work, the polymer mixed matric membrane that integrated with bio-additive nanoparticles (AgNPs) has shown a good strength and better particles distribution inside the membrane. This strong structure will assist the membrane in resisting failure structure when exposing to the high permeation pressure. Futhermore the used natural sources can reduce usage of chemical that not only toxic to the environmental but also is an expensive materials.

1.3 Research objective

The aim of this research study is to fabricate a mixed matrix membranes incorporated with biological synthesis of AgNPs, characterize and test its performance for membrane separation process. The specific objective of this study as follows:

i. To assess the effect of *P. speciosa* extracts in synthesizing bio-AgNPs particles towards characteristic, properties and performance of the nano synthesized particles.

ii. To determine the interface structure and bonding between bio-AgNPs and matrix of PSF membrane

iii. To optimise the operating parameter in synthesizing AgNPs using bio-synthesized technique.

iv. To evaluate the characteristic, properties and performance of the polymer mixed matric membrane integrated with bio-AgNPs.

1.4 Research scope

In order to achieve the objective, the following scopes are outlined:-

i. Synthesize bio-AgNPs using leaves extract of *P. speciosa* as reducing and capping agent.
ii. Characterizing bio-AgNPs via UV-Vis spectroscopy (UV-Vis), Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR)
iii. Optimizing process conditions for AgNPs preparation using Response Surface Methodology (RSM) for different parameters which are weight of *P. speciosa* leaves, incubation time, and temperature.
iv. Investigating toxicity level of AgNPs using Zebra fish (*Danio rerio*) test.
v. Preparing polysulfone membrane blended with both silver nanoparticles (bio-AgNPs and AgNPs) and polyethylene glycol (PEG) as polymer additives.

vi. Investigating the effect of the studied parameters on the membrane performances with respect to the pure water flux and rejection of natural organic matter (NOM).

vii. Characterizing membrane via Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), and X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Porosity.

viii. Antibacterial activity test of the prepared membranes by agar diffusion method against *S.aureus* and *E. coli* bacteria.

ix. Investigating interaction between AgNPs with PSf membrane using Dynamic Mechanical Analysis and Inductive Coupled Plasma Mass Spectrometer.

1.5 Significant and novelty of research

In this work, the biosynthesized particle from extract plant that not only generate antibacterial properties, but also able to provide better interface area as it is coated with an organic compound. This organic compound has the potential to minimize or reduce the incompatibility problem between organic polymer membrane structures that embedded with inorganic particle. The use of biosynthesized particle coated with organic compound provides better interface area for binding mechanism.

Even though, some previous studies have reported the used of Ag substances as an antibacterial agent, however, there is still a lack of research that have focused on bio-AgNPs. Thus, an investigation on the use of leaves extract from *P. speciosa* as reducing agent for biosynthesis of AgNPs in membrane structure has not yet been reported on other previous studies. Even though, the research on nanoparticle has gained a lot of attention nowadays, but this inorganic additive has a weak interface problem, creating the possibility of leaching. The used of biosynthesis not only overcome the incompatible problem but the ability of natural plant extract to coat the synthesized particles with the tailored and desired characteristic that possessed by this plant. Hence, this research is highly significant towards investigating the biosynthesis of AgNPs using an aqueous leaves extract of *P. speciosa* that consisted highly chemical constituents of flavonoids and terpenoids which used as reducing agents. This biosynthesis also can generate finer particles that also can create homogenous distribution across the matrix membrane that minimize or avoid the membrane failure due weak bonding at interface structure. Last but not least, this approach able to reduce the use of toxic chemical which offer better technique in creating greener technology.

CHAPTER 2

LITERATURE REVIEW

This chapter discussed previous related works on membrane technology and membrane improvement that focus on the mixed matric membrane. The introduction of some additive in modifying membrane properties and performance was also included. Furthermore, the nanoparticles technology and biosynthesis of nanoparticles using plant extracts was further explored. Lastly, the membrane fabrication and modification has also been discussed.

2.1 Introduction to membrane technology

The interface between two phases acting as a selective barrier is referred to as membrane (Tolaymat *et al.*, 2010). In other words, membranes form a barrier for some substances and allow others to pass through. The membrane filtration process could be a pressure or vacuum-driven and uses a layer of porous material to eliminate unnecessary particles from a suspension. Figure 2.1 shows the basic principle of membrane separation. Membrane separation processes consumed less energy when compared to other methods due to the non-heating operation process.

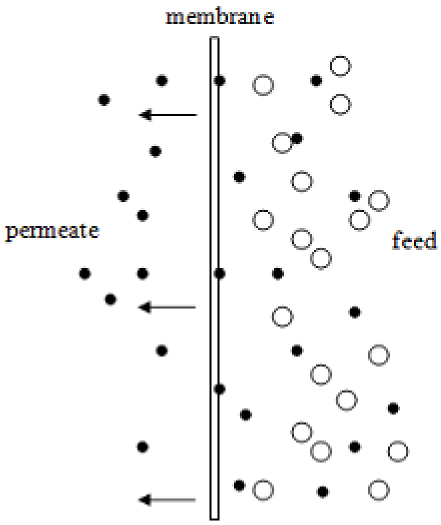

Figure 1.1: Basic principle of membrane separation.

The pressure driven operations involves four types of filtration process which are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The microfiltration can remove all contaminant particles from fluids or gases in the size range of 0.1 to 10.0 µm (1000 to 10,000 Å). Suspended solid and bacteria such as starch, *staphylococcus* bacteria and *pseudomonas diminuta* are some examples of filtrate substances treated by microfiltration process (Basri *et al.*, 2010). The microfiltration process involves two techniques, such as, (i) Cross-flow filtration, which is filtered tangentially across the membrane by the flow of the fluid and (ii) Dead-end filtration which is the most widely used. The commonly used operating pressure is in the range 0.02-0.5 MPa. While, the substances size within 100 to 1000 Å are commonly being removed from a suspension by ultrafiltration with operating pressure of about 0.3 MPa. The viruses, proteins and small colloidal natural organic matter were the common removal substances for ultrafiltration. The similarity between ultrafiltration and microfiltration process can be seen from their operation at low pressure, which is less than 200 kPa (Li *et al.*, 2013).

The nanofiltration pore size was smaller than microfiltration and ultrafiltration. The pore size from 1-10 Å is capable of removing multivalent ion such as calcium ion (Ca^{2+}) and magnesium ion (Mg^{2+}). Typical operating pressure for nanofiltration is higher compared to microfiltration and ultrafiltration, which is lying between 0.3-4.0 MPa. The nanofiltration membranes are composite membranes consisting of a carrier structure as well as a thin selective layer. Membranes with

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